## "On the Variation of the Electrical Resistance of Glass with Temperature, Density, and Chemical Composition." By THOMAS GRAY, B.Sc., F.R.S.E. Communicated by Professor Sir WILLIAM THOMSON, F.R.S. Received December 28, 1881. Read January 12, 1882.*

The following paper is a description of the methods adopted, and of the results obtained, in a series of experiments on the specific resistance of glass. These experiments were performed in the Physical Laboratory of the Imperial College of Engineering, Tokio, Japan.

An account of some preliminary experiments on this subject was communicated by the author of this paper to the "Philosophical Magazine" for October, 1880. In that paper attention was specially directed to the change of resistance with change of temperature, and to an apparently permanent change in electric quality which the glass underwent when subjected to a high temperature. Subsequent experiments have served to confirm the results there given, but shew that if the glass be newly made very little, if any, permanent change is brought about by heating.

In the experiments just referred to a current of electricity was kept flowing either continuously or at short intervals during the heating. As this might produce effects which would not be caused by heating alone, it was thought desirable to test one or two specimens for resistance at as low a temperature as possible, and then again, after the glass had been heated to between 200° and 300° C., and cooled to the same temperature. Experiments performed in this way have shown an exactly similar change to that previously obtained. It appears, therefore, that the change previously observed was due to heating.

The fact that the permanent change produced by heating to a high temperature was markedly greater in specimens of old than in specimens of new glass, rendered it probable that the change was due to some previous change in the opposite direction, which goes on slowly at the ordinary temperature. In order to put this conjecture to the test of experiment, advantage was taken of several specimens of newly-manufactured glass which had just been obtained from the Government Glass Works, Shinagawa, Tokio. The results of tests made on three specimens of that glass are given in the following table. The first two specimens were lime glass, while the third was a white semi-opaque flint glass, containing arsenic. In the first column the number of the specimen is written; in the second the resistance in ohms between two opposite faces of a cubic centimetre; in the third, the temperature at

* For abstract see *ante*, vol. 33, p. 256.

which the resistance was measured; in the fourth, the density of the glass; and in the fifth, the date at which the resistance was measured.

| No. of specimen. | Specific resistance in ohms per cub. centim. | Temperature. | Density. | Date. |
|---|---|---|---|---|
| 1 | $146 \times 10^{10}$ | 40° C. | 2·57 | May 3, 1880. |
| | $122 \times 10^{10}$ | ,, | ,, | December 9, 1880. |
| 2 | $24 \times 10^{10}$ | 40° C. | 2·53 | May 3, 1880. |
| | $17 \times 10^{10}$ | ,, | ,, | December 10, 1880. |
| | $12 \times 10^{10}$ | ,, | ,, | May 3, 1881. |
| 3 | $41 \times 10^{11}$ | 140° C. | 3·07 | May 17, 1880. |
| | $17 \times 10^{11}$ | ,, | ,, | November 17, 1880. |

These results show a very considerable increase of conductivity with age, and also show a marked difference in the variation of different specimens. The number of experiments is not sufficient to give much information regarding this time change, but the fact that they give evidence that such a change takes place seems to warrant the publication of these preliminary results.

The measurements of resistance described in this paper were, like those in the previous paper above referred to, for the most part made by means of an astatic galvanometer of high resistance and great sensibility. The galvanometer used had an internal resistance of 10,000 ohms, and one Daniell's element produced a deflection of one division when a resistance of about $10^{11}$ ohms was in the circuit. The great advantage of the galvanometer over the electrometer method of measurement is its simplicity; the deflection being independent of the capacity of the circuit, provided no change is taking place in that capacity. In many cases, however, the resistance of glass at low temperatures cannot be measured by the galvanometer, and in these cases, the most convenient instrument is a Thomson's quadrant electrometer.

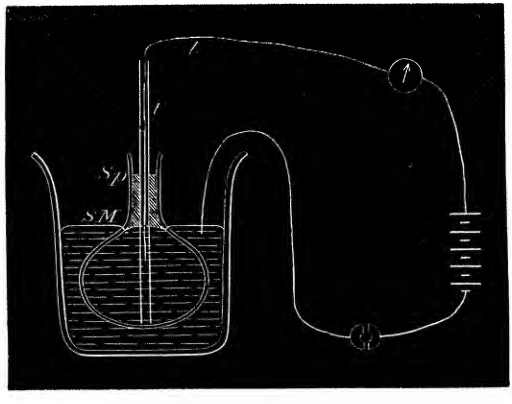
The method adopted in the galvanometer measurements was that of direct deflection, the current being produced by fifty Daniell's elements, placed on a table well insulated with ebonite supports, kept dry by being enclosed in boxes containing sulphuric acid. The main difficulty in this method is to ensure absence of leakage currents through the galvanometer. The test used for the absence of such currents was to insulate the electrode of the inside coating of the glass vessel, and then close the key. If there was no deflection, it was assumed that the circuit was sufficiently insulated.

Several measurements were made by means of the quadrant electrometer, and in that case the method adopted was to connect one coating of the glass, one pair of quadrants, and the case of the elec-

trometer to earth; while the other coating of the glass and the remaining pair of quadrants were connected together but insulated. The resistance was then calculated from the capacity of the glass vessel and electrometer quadrant, and the rate of loss of charge.

The conducting coatings for the glass were generally made by partly filling the vessel to be experimented on with mercury, and then immersing it in another vessel of mercury until the surface of the mercury inside and outside the vessel was at the same level. In order to avoid leakage over the sides of the vessel, it and the mercury were made thoroughly dry by heating, and when sufficiently cooled, a coating of paraffin was run over the surface of the mercury and the vessel. Through this coating of paraffin a fine glass tube, well dried and paraffined, was passed, thus furnishing at the same time a passage, and more thorough insulation against surface leakage for the electrode which made contact with the mercury. This explanation will be more readily understood by the aid of fig. 1, which shows the arrangement for measuring the resistance of a glass globe, the galvanometer, battery, and key being shown symbolically. In the figure SM repre-

Fig. 1.




sents the surface of the mercury, S*p* the surface of the paraffin, and *t* the fine tube through which the electrode, *l*, passes. The tube, *t*, and the neck of the globe were in such a case coated with paraffin.

The precautions against leakage here described are more necessary when the resistance at ordinary temperature is to be measured, but even in other cases it was found advisable to begin with this, and simply allow the paraffin to evaporate at high temperatures. The surface of the hot glass remained afterwards perfectly dry.

Sulphuric acid was sometimes used instead of mercury, and answers perfectly if the temperature does not require to be high. If, however,

the temperature requires to be raised until the acid evaporates, it becomes extremely disagreeable. The acid has the advantage that it keeps the vessel dry, and hence is to be preferred for low temperature measurements.

Abridged tables of results for a few characteristic specimens are annexed, and serve to illustrate the very wide range of resistance which may be obtained by using different specimens of glass. The variation with temperature of several specimens is illustrated by means of curves. These curves only show the variation with temperature through a small range, as it was found almost impossible to include both a number of curves and long range of temperature in the same diagram.

It will be observed on examining these curves that the rate of variation with temperature is very nearly the same, not only for different specimens of the same kind of glass, but for all the kinds of glass there figured. Other specimens, not included in this diagram, gave a very similar variation. On an average it may be said that the specific resistance of glass is halved for every 8°·5 C. rise of temperature.*

In the tables of results the density of each specimen is recorded, and in some cases the chemical composition also. The chemical analyses were performed in the Chemical Laboratory of the Imperial College of Engineering, Tokio, by Messrs. Fujii and Shimidzu, under the superintendence of Dr. Edward Divers, to whom the author is much indebted for the great interest he has taken, and assistance he has given, in the carrying out of these experiments.

It is very interesting to notice how very closely a change of density in flint glass agrees with a change of electrical resistance, and also that the electrical resistance of this kind of glass increased regularly until the density reached that point at which the composition of the glass was almost exactly that required for a trisilicate of lead, potash, and silica. The very high density of lead oxide causes the density of the glass to be an indication of the quantity of lead present, and

* Note added April 26, 1882.—Although the fall of resistance with rise of temperature generally follows very nearly the logarithmic law, the results show variations from that law which I am not yet able to explain. The resistance at high temperatures is generally higher than would be inferred from the resistance and rate of variation at low temperatures. It is remarkable that specimens which had a high resistance gave results more nearly in agreement with the logarithmic law than specimens of comparatively low resistance.

The resistances quoted in the tables are those calculated from observations after one minute's electrification, the direction of the current being alternately in opposite directions, and only allowed to flow for about one minute at each observation. The method of observation was thus similar to that described as "the first method" in my paper in the "Philosophical Magazine" above referred to. (See "Phil. Mag.," October, 1880, page 227.)

hence the density in this case serves as a guide to the electrical quality of the glass. A specimen of glass containing too much lead for a pure silicate has not yet been experimented on, but the result of such an experiment would be of great interest in furnishing evidence as to whether purity of chemical composition and high electrical resistance go together.

When we turn to lime glass, however, we find that the density is no guide to the electrical quality. Specimens having nearly the same density vary enormously as to their electrical resistance. This, however, is to be expected, as the density may change but little, even when the chemical composition is greatly altered. Lime glass generally contains both soda and potash, and the ratio of these two bases may influence considerably the density, while the glass remaining a good glass the electrical conductivity may not be much affected.

So far as the results of chemical composition go, however, it appears that in the case of lime glass also, a glass which would be pronounced good from a chemical point of view is also relatively good from an electrical point of view. On the other hand a glass which would be pronounced bad chemically is also bad electrically.

In the following tables the resistance at various temperatures of six specimens of lime glass and two specimens of lead glass are given. The first column contains the temperature, the second the resistance in ohms of a cubic centimetre, the third the density, and the fourth the chemical composition in those cases where it was determined.

Specimen I. (Bohemian glass tubing.)

| | | | |
|---|---|---|---|
| 60° C. | ..... | ..... | 2·43 |
| 100 | ..... | $20 \times 10^{11}$ | |
| 130 | ..... | $20 \times 10^{10}$ | |
| 160 | ..... | $24 \times 10^{9}$ | |
| 174 | ..... | $87 \times 10^{8}$ | |

Specimen II. (Test-tube.)

| | | | |
|---|---|---|---|
| 37° C. | ..... | ..... | 2·458 |
| 59 | ..... | ..... | |
| 73 | ..... | ..... | |
| 101 | ..... | ..... | |
| 131 | ..... | ..... | |

Specimen III. (Japanese lime glass tubing.)

| | | | | |
|---|---|---|---|---|
| 10° C. | .. | $670 \times 10^{10}$ | .. | 2·55 |
| 30 | .. | $199 \times 10^{10}$ | .. | .. |
| 52 | .. | $300 \times 10^{9}$ | .. | .. |
| 75 | .. | $450 \times 10^{8}$ | .. | .. |
| 85 | .. | $220 \times 10^{8}$ | .. | .. |

| | |
|---|---|
| Silica..... | 61·3 |
| Potash..... | 22·9 |
| Lime, &c., by diff. | 15·8 |
| | 100·0 |

Specimen IV. (Japanese lime glass tubing.)

| | | | | |
|---|---|---|---|---|
| 35° C. .. | $113\times10^{11}$ .. | 2·499 .. | Silica ..... | 57·2 |
| 55 .. | $25\times10^{11}$ .. | .. .. | Potash ..... | 21·1 |
| 75 .. | $61\times10^{10}$ .. | .. .. | Lime, &c., by diff. | 16·7 |
| 85 .. | $26\times10^{10}$ .. | .. .. | | |
| 95 .. | $12\times10^{10}$ .. | .. .. | | 100·0 |

The analyses of the last two specimens are only approximate, having been made previous to the electrical experiments, and for a different purpose. The composition differs very widely from that which is required for a pure silicate, and the electrical resistance is also found to be very low.

Specimen V. (French flask.)

| | | | | |
|---|---|---|---|---|
| 45° C. .. | $327\times10^{10}$ .. | 2·533 .. | Silica ..... | 70·05 |
| 55 .. | $133\times10^{10}$ .. | .. .. | Lime..... | 10·33 |
| 65 .. | $509\times10^{9}$ .. | .. .. | Lead oxide ..... | 2·70 |
| 75 .. | $204\times10^{9}$ .. | .. .. | Soda..... | 14·32 |
| 86 .. | $812\times10^{8}$ .. | .. .. | Potash ..... | 1·44 |
| 95 .. | $391\times10^{8}$ .. | .. .. | Magnesia..... | 0·10 |
| 108 .. | $133\times10^{8}$ .. | .. .. | Alumina, iron oxide, | |
| 117 .. | $707\times10^{7}$ .. | .. .. | manganese oxide . | 1·45 |
| | | | | 100·39 |

With regard to this specimen, Dr. Divers writes as follows:—

"This seems to be a soda lime glass mixed with a little potash lead glass; the latter having been thrown in as cullet. Assuming this to be the case, we will have approximately—

| | |
|---|---|
| Potash lead glass ..... | 8·7 |
| Soda „ ..... | 91·3 |
| | 100·0 |

The soda lime glass has then the composition—

| | |
|---|---|
| Silica ..... | 72·7 |
| Lime..... | 11·4 |
| Soda..... | 15·9 |
| | 100·0 |

Apparently the best glass has the formula—

$$CaO,Na_2O,\underset{6}{SiO_2} = \begin{cases} \text{Silica} \ldots\ldots & 75{\cdot}3 \\ \text{Lime} \ldots\ldots & 11{\cdot}7 \\ \text{Soda} \ldots\ldots & 13{\cdot}0 \end{cases}$$

100·0

"If this is deviated from an increase in the proportion of soda to lime requires a considerable increase in the proportion of silica to base. The flask is therefore defective, for not only is the soda in excess to the lime, but the silica is deficient. I calculate that from 20 to 25 parts of silica should be added to 100 of that glass to counteract the excess of soda. Such a glass would be—

| | |
|---|---|
| Silica | 77·5 |
| Lime | 9·5 |
| Soda | 13·0 |

"However, too little is yet known of the relations of composition to quality of glass to admit of positive statement.

"The empirical formula $x\overline{CaO,SiO_2} + y\underset{5}{\overline{Na_2O,SiO_2}}$ seems to me to be a tolerably accurate expression of the various kinds of good glass, provided $x$ and $y$ are not very different from one another. When equal, the glass is certainly excellent."

Specimen VI. (Bohemian beaker.)

| | | | | |
|---|---|---|---|---|
| 66° C. | $497\times10^{11}$ | 2·587 | Silica | 75·65 |
| 88 | $828\times10^{10}$ | .. | Lime | 8·48 |
| 110 | $138\times10^{10}$ | .. | Potash | 7·92 |
| 132 | $230\times10^{9}$ | .. | Soda | 6·92 |
| 150 | $540\times10^{8}$ | .. | Magnesia | 0·36 |
| 170 | $147\times10^{8}$ | .. | Alumina, iron and | |
| 193 | $308\times10^{7}$ | .. | manganese oxides. | 0·70 |
| | | | | 100·03 |

Assuming the formula $K_2O,CaO\underset{6}{SiO_2} + Na_2O,CaO,\underset{6}{SiO_2}$, as giving the best composition, we should have—

| | | | |
|---|---|---|---|
| Potash | 18·4 | Soda | 13·0 |
| Lime | 11·0 | Lime | 11·7 |
| Silica | 70·6 | Silica | 75·3 |

The mean of which would give—

| | |
|---|---|
| Potash | 9·2 |
| Soda | 6·5 |
| Lime | 11·3 |
| Silica | 73·0 |

The alkali is therefore slightly in excess, but to compensate that, there is an excess of silica, the result being a very good glass, both chemically and electrically.

Specimen VII. (Arsenic-enamel glass.)

| | | | | | |
|---|---|---|---|---|---|
| 49° C. | $140\times10^{13}$ ? | 3·07 | Silica | | 54·2 |
| 105 | $230\times10^{11}$ | | Lead oxide | | 23·9 |
| 115 | $101\times10^{11}$ | | Potash | 17·5 | *10·5 |
| 125 | $45\times10^{11}$ | | Soda | | * 7·0 |
| 135 | $22\times10^{11}$ | | Lime | | 0·3 |
| | | | Magnesia | | 0·2 |
| | | | Iron and manganese oxide and alumina | | 0·4 |
| | | | Arsenic oxide by diff. | | 3·5 |
| | | | | | 100·0 |

In this glass we have an excess or alkali for the lead oxide, and a deficiency of silica; the composition is rendered complicated, however, by the presence of the arsenic.

Specimen VIII. (Thomson's electrometer jar.)

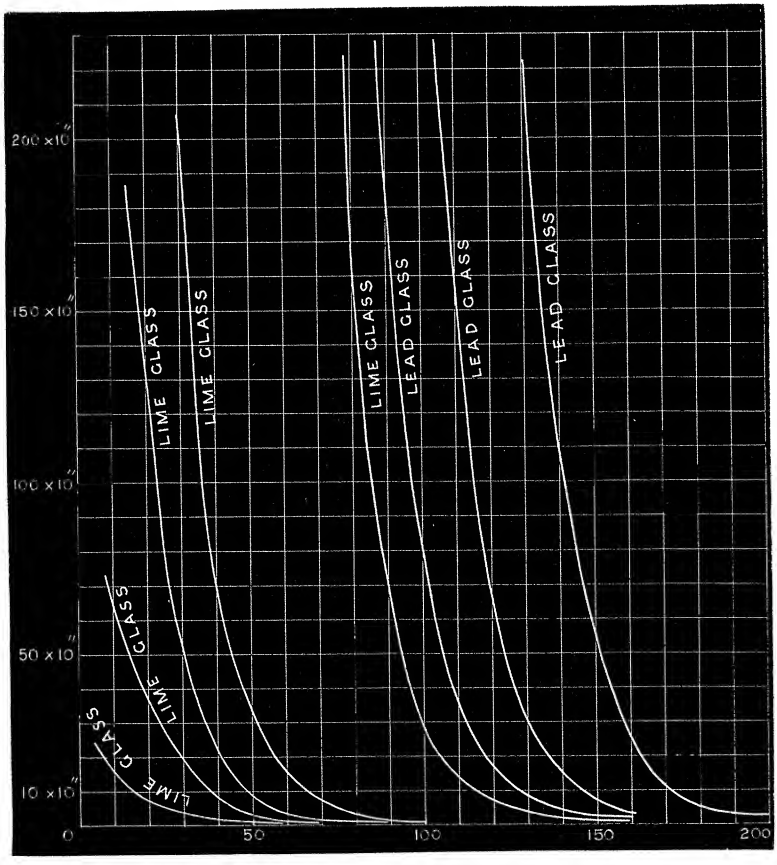
| | | | | |
|---|---|---|---|---|
| 100° C. | $206\times10^{12}$ | 3·172 | Silica | 55·18 |
| 120 | $468\times10^{11}$ | | Lead oxide | 31·01 |
| 140 | $106\times10^{11}$ | | Potash | 13·28 |
| 160 | $245\times10^{10}$ | | Lime | 0·35 |
| 180 | $56\times10^{10}$ | | Magnesia | 0·06 |
| 200 | $12\times10^{10}$ | | Alumina, iron and manganese oxides. | 0·67 |
| | | | | 100·55 |

The formula $PbO,K_2O,\frac{SiO_2}{6}$, gives—

| | |
|---|---|
| Silica | 53·2 |
| Lead oxide | 32·9 |
| Potash | 13·9 |

* Ratio of potash to soda may be too high.

FIG. 2.




Allowing the lime, magnesia, &c., to replace one equivalent of lead oxide, this glass very nearly agrees with the above theoretical composition. This therefore ought to be an excellent glass, and so it turns out to be electrically. So far as these results go then, the evidence is in favour of an exact chemical compound for a glass of low conductivity.

In the following table, the resistances at 60° C. of numbers of different specimens of lime glass are given, together with their densities. The first column tells the kind of vessel experimented on; the second the resistance in ohms of a cubic centimetre, and the third the density.

| Description of glass vessel. | Resistance in ohms per cub. centim. | Density. |
|---|---|---|
| Bohemian tubing .... | $605\times10^{11}$ .... | 2·430 |
| ,, beaker.... | $425\times10^{11}$ .... | 2·427 |
| ,, ,, .... | $542\times10^{11}$ .... | 2·454 |
| ,, ,, .... | $715\times10^{11}$ .... | 2·587 |
| Florence flask..... | $469\times10^{9}$ .... | 2·523 |
| French ,, ..... | $996\times10^{9}$ .... | 2·533 |
| Japanese globe..... | $210\times10^{10}$ .... | 2·510 |
| Test-tube..... | $144\times10^{9}$ .... | 2·435 |
| ,, ..... | $350\times10^{9}$ .... | 2·44 |
| ,, ..... | $285\times10^{10}$ .... | 2·458 |
| ,, ..... | $125\times10^{9}$ .... | 2·467 |
| * ,, ..... | $147\times10^{10}$ .... | 2·499 |
| * ,, ..... | $364\times10^{8}$ .... | 2·53 |
| * ,, ..... | $155\times10^{9}$ .... | 2·55 |
| * ,, ..... | $374\times10^{9}$ .... | 2·57 |
| ,, ..... | $196\times10^{9}$ .... | 2·667 |
| * ,, ..... | $933\times10^{9}$ .... | 2·547 |

The specimens marked (*) were of Japanese manufacture; the first four being potash lime glass, and the last soda lime glass. The other test-tubes were supplied from England, and were probably German white glass.

The next table contains a similar comparison for a few specimens of flint glass. The columns have the same meaning as in the last table.

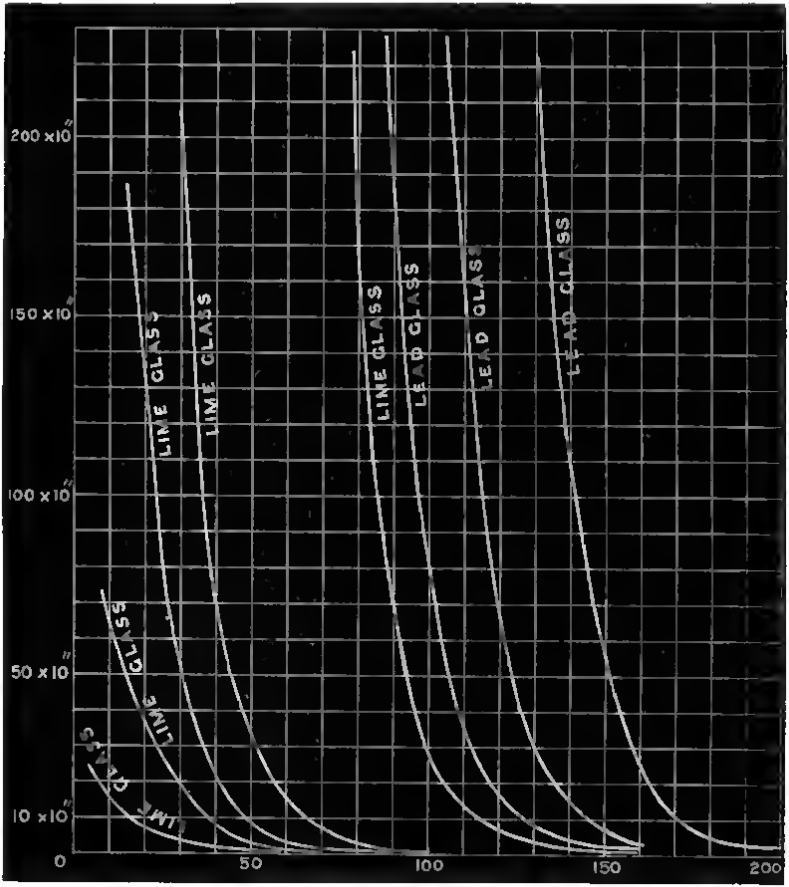
| | | | |
|---|---|---|---|
| Tumbler of toughened glass... | $622\times10^{10}$ | .. | 2·670 |
| Piece of tubing..... | $389\times10^{11}$ | .. | 2·753 |
| Japanese globe..... | $120\times10^{12}$ | .. | 2·840 |
| Cylindrical cup with hemispherical base of arsenic-enamel glass..... | $302\times10^{12}$ | .. | 3·070 |
| A Thomson's quadrant electrometer jar..... | $102\times10^{13}$ | .. | 3·172 |

"On the Causes of Glacier-Motion." By WALTER R. BROWNE, M. Inst. C.E., late Fellow Trin. Coll., Cambridge. Communicated by Professor STOKES, Sec. R.S. Received June 1. Read June 15, 1882.

The question of the causes which produce the movement of glaciers, which was at one time so eagerly discussed, would appear to have slumbered for the last ten years. This cannot be said to arise from

Fig 1

FIG. 2.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